

## RAW MATERIALS

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### NATURE OF THE LIQUEFACTION AND FLUIDITY OF KAOLIN FROM THE ZHURAVLINYI LOG DEPOSIT (REVIEW)

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Studies of the nature of the most effective methods of regulating the liquefaction and fluidity of kaolin from the Zhuravlinyi Log deposit are reviewed. Data on the material, mineral, and microaggregate compositions of different types of kaolin as well as the particulars of the morphology and crystal-chemical properties of kaolinite are presented. It is shown that kaolin microaggregates consist of a mixture of kaolinite of different sizes — from large to small with average degree of ordering, right up to ultrafine and x-ray amorphous.

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**Key words:** kaolin, kaolinite, halloysite, liquefaction, fluidity, morphology, defects.

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At present the Zhuravlinyi Log deposit is practically the only domestic source of kaolin-containing materials with proven reserves of eluvial kaolins. The suitability of kaolin as the main component of ceramic mix is determined, on the one hand, by the technological properties of slip and ceramic mix based on it and, on the other hand, by the coloristic properties of ceramic articles. According to its coloristic gradation [1] kaolin can be used for the production of high-quality porcelain with high whiteness as well as for sanitary and building ceramic. However, enriched kaolin for the production of ceramic articles by means of casting is of limited use because of poor liquefaction and fluidity of the slip [2, 3].

For purposes of studying the reasons for the poor liquefaction of kaolin from the Zhuravlinyi Log deposit (ZLD) and the poor fluidity of suspensions based on it, the material, mineral, and particle-size compositions of kaolin as well as the structural and crystal-chemical particulars of kaolinite were analyzed.

From the moment ZLD began operations the main work concerned the study of the mineral composition and its effect on the technological properties. A systematic study of the mineral composition of kaolin raw material and the crystal-chemical particulars of kaolinite to confirm the reserves at the Glebychev Ceramics Works of the Russian Federation was performed at the Central Scientific–Research Institute Geolnerud in Kazan<sup>2</sup>. Subsequently, the technological sci-

tific–research work was based on these results. Specifically, the poor liquefaction of kaolins from Zhuravlinyi Log was attributed to the presence of halloysite in them. However, in the course of the operation of the deposit it became necessary to perform additional work, which showed that together with this ultrafinely dispersed particles of kaolinite as well as the presence of a smectitic component and aluminosilicate gel can have a similar effect. The studies of kaolinite performed under the direction of R. Kitagawa at the University of Hiroshima have confirmed that halloysite is undeveloped in the ZLD kaolins, while smectites are widely disseminated in them but in negligible quantities.

Work performed in recent years has shown that there is a direct relationship between the composition of biota together with the products of their metabolism and the technological properties of kaolin.

Natural types of green kaolin are distinguished by their textural and structural features reflecting the formation method [4]: clayey rocks in which the relict texture and structure — granite, pegmatite, and gneiss — is preserved are classified as eluvial; rocks in which relict structure is not seen are classified as diluvial (re-deposited kaolin). The eluvial weathering crust along leucocratic granites and gneisses is the predominate form found at the ZLD deposit. Diluvial deposits occur sporadically in the form of pockets at the top of the weathering crust.

Three types of principal industrial-technogenic kaolins are distinguished according to chemical composition:

– A — normal kaolin according to leucocratic granites; content  $K_2O + Na_2O < 1.5\%$ ;

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**TABLE 1.** Mineral Content after Primary Enrichment

Kaolin type	Content, wt. %			
	Kaolinite	Feldspar	Quartz	Mica
A	87 – 91	< 2.2	5 – 8	2 – 3
B <sub>1</sub>	71 – 81	10 – 16	6 – 9	4 – 6
B <sub>2</sub>	66 – 76	15 – 20	6 – 9	4 – 6
C	80 – 90	1 – 2	6 – 9	4 – 6

– B<sub>1</sub> and B<sub>2</sub> — alkaline kaolins according to leucocratic granites; content K<sub>2</sub>O + Na<sub>2</sub>O > 1.5%; the fraction < 63  $\mu$ m comprises 50% (B<sub>1</sub>) and 2% (B<sub>2</sub>);

– C — kaolin according to gneisses (apogneiss).

Alkaline kaolins are developed at the bottom of the profile of the weathering crust [5].

**Differences between Different Types of Kaolins with Respect to Mineralogical Composition.** With respect to the principal rock-forming minerals, as determined by the x-ray diffraction ZLD kaolins of different types are similar and consist of quartz, kaolinite, microcline, and hydrated muscovite (in apogneiss — muscovite and biotite) in different ratio for different types. The content of the principal minerals in green kaolin material varies considerably (wt.%): 30 – 70 kaolinite, 30 – 50 quartz, 1 – 18 potassium feldspar, 3 – 9 mica. After primary granulometric enrichment of different types of kaolins their content of kaolinite increases as a result of large aggregates of quartz, feldspar, and mica being sifted out (Table 1).

Montmorillonite as an independent mineral phase is encountered in negligible quantities in single samples. However, subsequent studies revealed the presence of a smectitic phase [6]. Halloysite 10Å has been determined in single cases in re-deposited kaolins by means of x-ray diffraction.

X-ray diffraction analysis makes it possible to distinguish two forms of halloysite 10Å — halloysite proper (with the first basal reflection near 9.8 and 10 Å) and 7Å — metahalloysite (with the first basal reflection 7.3 – 7.6 Å), which is a product of partial degradation of halloysite [7]. It should be underscored that the term “halloysite” is applicable exclusively to tubular particles containing molecular water within their structure.

In samples of different types of ZLD kaolin the first basal reflection of kaolinite near 7.2 Å is ordinarily asymmetric with a distinct shoulder 7.4 – 7.8 Å, which can be ascribed to halloysite 7Å [6]. Parameters that make it possible to identify the individual reflection of halloysite and evaluate its relative amount, which with respect to kaolinite is approximately 5 – 10%, were obtained during mathematical processing of the diffractions patterns using software in a manual regime. It should be noted that an increase of the interplanar separation can attest to the presence of kaolinite in the form of disordered occurrence of layers with a large basal distance, for example, smectitic kaolinites or kaolinites

containing molecular water. The shape of the first basal reflection is different in different samples.

The thermal behavior of the kaolin samples was conducted in the temperature interval 30 – 1200°C using a Netzsch STA 409PC Luxx synchronous thermal analyzer. An endothermal effect in an approximate interval 30 – 200°C with mass loss 0.56 – 2.27%, indicating the presence of water molecules, possibly associated with the presence of halloysite, mixed-layered minerals with smectite layers, or aluminosilicate gels, is recorded for all experimental samples. In the temperature interval 490 – 780°C, a distinct endothermal effect peaking at temperature 542 – 550°C, associated with the amorphization of kaolinite, is recorded for all samples. In most samples a weak endothermal effect, which is not accompanied by a distinct mass loss, is recorded in the interval 930 – 950°C; this effect could be due to the destruction of the mica structure and the formation of melt due to ultrafine particles and aluminosilicate gels. An exothermal effect peaking at temperature 1004 – 1011°C is recorded at high temperatures, 950 – 1038°C; this effect is due to the crystallization of mullite.

Electron-microscopic studies show that two types of elongated particles — planar particles 20 – 100  $\mu$ m in size and tubular crystal to 6  $\mu$ m are present in the ZLD kaolins. Only the tubular crystals can be regarded as halloysite [7]. According to studies performed by the authors, the total amount of tubular precipitates is small and less than 1 vol.% of the total number of particles, along which clump-like precipitates predominate.

It is noted in [8] that the halloysite content is higher in alkali kaolinites than in normal kaolins. The largest amount of halloysite is found in apogneiss (type C) and re-deposited (diluvial) kaolins.

Comparing data from optical and x-ray analysis showed that the term halloysite applied to ZLD kaolins is imprecise. On the one hand the content of classic tubular halloysite is negligible in high-quality samples and cannot give individualized reflections in diffraction patterns. On the other hand in practically all diffraction patterns the form of the first basal reflection of kaolinite is complicated by a shoulder in the low-angle region that can be identified as halloysite 7Å.

Thus, despite its negligible amount it is precisely the presence of halloysite that is one of the reasons for the instability of the technological parameters of kaolins [6]. This explains the high absorption power indicators on the one hand and the poor liquefaction and fluidity of kaolin on the other. In addition, smectite was found in kaolin samples; this undoubtedly promotes an increase of its absorption power.

**Microaggregate Composition of Kaolin and Kaolinite Morphology.** The sizes of the aggregates and structural-morphological features of kaolinite are basic indicators affecting the rheological properties of a kaolin suspension. The microaggregate composition of four natural types of kaolin A, B<sub>1</sub>, B<sub>2</sub>, and C (< 63  $\mu$ m size fraction) separated on a sieve was determined by the sedimentation method following

GOST 23905. The presence of aggregates of different strength can be established according to the degree of their disaggregation by a 4% solution of sodium pyrophosphate. Strong microaggregates withstand such treatment [9]. ZLD kaolins of different natural types are distinguished according to the size of the aggregates — type A and especially gneiss type C kaolins have on average a high yield for all four fractions  $< 20$ ,  $< 10$ ,  $< 5$ , and  $< 2$   $\mu\text{m}$  as compared with  $B_1$  and  $B_2$  type alkaline kaolins. Therefore, on average the aggregate size for alkaline kaolin is larger than for normal kaolin. It can be supposed that the alkaline kaolins largely withstand this treatment and, correspondingly, have stronger interparticle contacts. The contact strength is explained by the type of contacts on the one hand and by the crystal sizes on the other.

Electron-microscopic studies of kaolin have revealed a difference in the sizes of kaolinite between samples of different natural types:

- normal kaolin (A) is represented by kaolinite crystals ranging in size from 0.5 to 1.5 – 2.0  $\mu\text{m}$ ; their shape is pseudohexagonal isometric and less often thin-plate-like with sharp contours; smaller particles lose their profile and contour sharpness; large aggregates are present;
- gneiss kaolins (C) and alkali kaolins ( $B_1$  and  $B_2$ ) consist of smaller kaolinite crystals with pseudo-hexagonal shapes 0.2 – 1.0  $\mu\text{m}$  in size, often of fragmentary type, more prone toward aggregation.

Examination of ZLD kaolinite using a Phillips CM 12 transmission electron microscope with pictures of the microstructure being obtained showed a clear particle-size dependence of the morphological parameters and the structural order of kaolinite [10]. The especially noticeable changes are associated with the fine fractions, starting at 10  $\mu\text{m}$ ; the most sharply manifested changes occur in the  $< 0.5$   $\mu\text{m}$  fraction. Hexagonal kaolinite crystals with grain size  $(4 - 4.5) \times (6 - 7)$   $\mu\text{m}$  are characteristic for the 5 – 10  $\mu\text{m}$  kaolin fraction, hexagonal with 1 – 3 and 0.6 – 0.8  $\mu\text{m}$  edges 1 – 5 and 0.5 – 1.0  $\mu\text{m}$ , respectively. If almost ideal microdiffraction patterns with a hexagonal intensity distribution were obtained for 5 – 10 and 1 – 5  $\mu\text{m}$  fractions, pseudo-hexagonal motifs of reflections were obtained for the 0.5 – 1.0  $\mu\text{m}$  fraction while typical powder patterns were obtained for the  $< 0.5$   $\mu\text{m}$  fraction. Kaolinite particles  $< 0.5$   $\mu\text{m}$  are characterized by almost complete absence of sharp boundaries and the lowest perfection and degree of arrangement on the boundary of the crystalline state, but complete amorphousness is not observed. For this reason it can be assumed that particles or blocks of kaolinite, determined by size as ultrafine, i.e., comparable in size to x-ray wavelengths, are present in ZLD kaolin [11]. The ultrafiness of kaolinite results in a change of its structural state and an increase of the sizes of kaolin microaggregates.

Thus, different types of kaolins are distinguished by the microaggregate composition: alkaline kaolins of different fractions as compared with normal kaolin have on average

larger aggregates. Since microaggregates are not broken down by sodium pyrophosphate, this attests to strong nature interparticle contacts. Kaolinite sizes vary in a wide range right up to sizes comparable to the ultrafiness and boundaries of the amorphous state.

**Structural and Crystal-Chemical Particularities of Kaolinite.** The degree of structural perfection of kaolinite has a large effect on the rheological properties of kaolin suspensions: the higher the index of crystallinity of kaolinite, the better the liquefaction of kaolins.

Several methods have been proposed to make a quantitative assessment of the degree of structural perfection of kaolinite. These methods are based on the use of different resolution and changes in definite reflections in the x-ray diffraction patterns [12, 13] and on the line intensities in the electron paramagnetic resonance spectrum (EPR) [14 – 16]. Diffraction methods are used to reveal and analyze long-range order in the structure of kaolinite, while aside from determining the crystallinity index EPR spectroscopy makes it possible to identify point defects, including point substitution defects and electron – hole centers (EHC).

Usually, the Hinckley index  $\chi_R$  is used to determine the degree of structural perfection of long-range order in kaolinite. The differences in the degree of long-range order can be due to different factors — displacement of the adjoining layers relative to one another, presence of dislocations, presence of water molecules in the interlayer positions, and so forth [15]. The value of  $\chi_R$  for kaolinite fractions from  $< 63$  to  $< 20$   $\mu\text{m}$  varies from 0.61 to 1.12 and characterizes the structure of kaolinite on average as medium-perfect. In the interval of these values of  $\chi_R$  for kaolinite of normal kaolin varies from 0.87 to 1.12, exceeding the corresponding values for kaolinite of alkaline kaolin (from 0.61 to 0.91). If  $\chi_R$  is related with the degree of structural ordering of kaolinite, the reciprocal values of the half-width of the reflection  $d_{001}$ , whose values are measured in degrees  $\theta$ , characterize the sizes of kaolinite crystallites along the  $c$  axis ( $\chi_D$ ). The indices  $\chi_R$  and  $\chi_D$  for granite and gneiss kaolins (type A and C) are larger than the corresponding indices of alkaline kaolin (types  $B_1$  and  $B_2$ ). In all kaolins of different natural types, as the fractional size decreases from  $< 63$  to  $< 20$   $\mu\text{m}$ , the indices  $\chi_D$  and  $\chi_R$  decrease. Therefore, kaolinite in fine fractions possesses smaller crystallites and is more defective. Comparing data from electron microscopy and x-ray diffraction confirms the results of [7], according to which poorly crystallized kaolinite is encountered in the form of irregularly formed hexagonal flakes and possesses smaller crystals. Thus, the crystallinity indices and crystallites of kaolinite in normal kaolin are larger than in alkaline kaolin.

The room-temperature EPR spectra of kaolinite in kaolin samples of different fractions were recorded with a RE-1306 radiospectrometer at frequency 9370 MHz. Two types of paramagnetic defects have been found in ZLD kaolins: paramagnetic iron ion  $\text{Fe}^{3+}$  impurity and EHC. Correspondingly,

several groups of signals are distinguished in the EPR spectrum:

- a wide signal in the range  $g \sim 2.0 - 3.0$  is associated with iron oxides adsorbed on the surface of kaolinite and with particles of iron minerals;
- a series of lines in the region  $g \sim 2.0$  is formed by at least three different EHC.

The wide, asymmetric signals with  $g$ -factor in the range  $2.0 - 3.0$  are characteristic for iron with different structural organization — from molecular-cluster and supermagnetic to the crystalline state of iron minerals [18]. Unfortunately, this method cannot be used to determine which iron fraction is found in the form of minerals in the rock volume and which is adsorbed on the surface of kaolinite, forming phase contacts between particles with formation of strong aggregates.

Of special significance among point defects are substitution defects  $\text{Fe}^{3+} \rightarrow \text{Al}^{3+}$ , since iron is the principal impurity in natural kaolins [19] and, as assumed, affects the degree of ordering of kaolinite and the particle sizes. An extensive study of the EPR spectra of  $\text{Fe}^{3+}$  for kaolinite has been performed [14 – 16, 18 – 24]. It is shown in [15] that the EPR signals in a weak magnetic field  $g \sim 4.0$ , which were recorded in the form of a triplet, are ordinarily interpreted as a superposition of the spectra of two centers: Fe(I) center — central line with  $g \sim 4.27$  and Fe(II) center with side lines with  $g$  values 4.9, 3.7, and 3.5. There is no single opinion concerning the structural position of  $\text{Fe}^{3+}$  ions. Most researchers assume [15] that the two centers Fe(I) and Fe(II) correspond to the substitution  $\text{Fe}^{3+} \rightarrow \text{Al}^{3+}$  at the octahedral position of the kaolinite layer, which differ by the crystal field and different degree of distortion. Other researchers show [20] that the central line of the Fe(I)-center belongs to  $\text{Fe}^{3+}$  in tetrahedral positions inside crystallites and on the basal surfaces: the outer lines of a Fe(II)-center are due to the substitutions  $\text{Fe}^{3+} \rightarrow \text{Si}^{4+}$  on the side surfaces of the kaolinite particles. It has also been shown [15] that these signals could be associated with stacking faults, the presence of layer of dickite or perturbations due to radiation damage. Luminescence spectroscopy has revealed uranyl impurities in ZLD kaolin [21]; these impurities can produce structural defects and EDC as a result of radiation emission. Thus, the intensity of different EPR signals and therefore the concentration of the corresponding defects in kaolinite can vary considerably from one kaolin sample to another.

The relative contributions of both types of centers Fe(I) and Fe(II), differing by the intensity of the EPR signals, to the degree of ordering in kaolinite has been demonstrated in [22]: ordered kaolinite with average specific surface area shows the strongest signal at the position of the Fe(II) center, while disordered kaolinite with a large specific surface area shows the same in the position of the Fe(I) center. According to [23], the relation  $\text{Fe(I)} > \text{Fe(II)}$  holds for ZLD kaolins. Therefore, kaolinite from this deposit is structurally less ordered and it can be assumed that it possesses the largest spe-

cific surface area. This supposition has been confirmed experimentally.

The EPR study of washed fractions of kaolinite with particles of different size (from 0.5 to 5.0  $\mu\text{m}$ ) showed [10] that the EPR signals due to the Fe(I) center remain unchanged while the Fe(II) signals broaden. The latter effect is due to the finest of the fractions studied, which is represented by particles of irregular shape, resembling fragments of hexagonal crystals.

The shape and intensity of the EPR signal due to the iron structure can be used as a sensitive indicator to explain the long-range order comparable to the values of the index  $\chi_R$ .

The value of the crystallinity index is calculated as the ratio of the sum of the intensities  $J$  of the peripheral lines of Fe(II) of the triplet EPR spectrum of  $\text{Fe}^{3+}$  ions to the intensity of the central line. Thus, this parameters is dimensionless [24]:

$$X_{\text{EPR}} = \frac{J_{3.7} + J_{4.9}}{J_{4.2}},$$

where  $J_{3.7}$ ,  $J_{4.2}$ , and  $J_{4.9}$  are the intensity values of the  $g$ -factor.

Compared with alkaline kaolin, normal kaolin has higher values of the kaolinite crystallinity index according to both the x-ray diffraction data  $\chi_R$  (0.89 – 1.12 for normal kaolin versus 0.68 – 0.91 for alkaline kaolin) and the EPR data,  $\chi_{\text{EPR}}$  (1.14 – 1.30 and 0.90 – 1.22, respectively).

At least three centers have been identified in the region  $g \sim 2.0$  [16]. Two are A and A' centers (trapped hole on oxygen in the Si–O band). Correspondingly, their orientation is parallel and perpendicular to the  $ab$  plane. The third one is a B center (hole on oxygen, binding Al in two adjoining octahedral positions  $\text{Al}_{\text{VI}}\text{O}^-\text{Al}_{\text{VI}}$ ). Heat treatment showed that the thermal stability of the centers decreases in the order  $A > A' > B$  in the temperature range to 450°C (the B center completely vanishes to 300°C; the A' center vanishes at 400°C in a time longer than 2 h; the A center is stable to 450°C) [15].

The EHC intensity in the EPR spectrum of ZLD kaolin varies over a wide range — from 0.50 to 1.40 with the values for granite kaolins predominating over the corresponding values of alkaline kaolin (0.90 – 1.40 and 0.50 – 1.08, respectively). It has been observed that the intensity of EHC of normal kaolin is higher than that for alkaline kaolin [23]. The intensity of EHC in the weathering profile of ZLD kaolin is an order of magnitude higher than for kaolin from the Chaimat [23] and Kovyl'noe [24] deposits. Such EHC are charge-compensated and do not disrupt the long-range order in the structure of kaolinite but do affect the sorption power of kaolinite.

It is known that as the crystallinity index and particle size of kaolinite decrease, the sorption power of the particles increases [25]. It has been shown that the particle size is the more significant indicator for the cationic exchange volume, since as particle size decreases, the charge along the broken



**TABLE 2.** Technological Properties of Different Types of Kaolin

Property indicators	Natural kaolin			
	A	B <sub>1</sub>	B <sub>2</sub>	C
Fractional yield, wt. %:				
< 20 $\mu\text{m}$	78.4	66.6	63.2	78.3
< 10 $\mu\text{m}$	65.3	54.3	50.6	67.6
< 5 $\mu\text{m}$	49.7	40.2	37.5	54.1
< 2 $\mu\text{m}$	36.9	29.3	27.5	42.0
Adsorption according to methylene blue, mg/g:				
fractions, < 63 $\mu\text{m}$	17.6	18.9	20.0	21.0
fractions, < 20 $\mu\text{m}$	21.0	23.5	24.5	25.2
Ultimate bending strength, MPa	1.85	2.44	3.16	2.85
Shrinkage, %	4.3	4.5	5.5	4.9

edges of the hexagonal plates increases more than in the case of charge due to the isomorphic substitution  $\text{Al}^{3+} \rightarrow \text{Si}^{4+}$  and determining the degree of structural ordering of kaolinite. For this reason, the edge sections of the crystals at the locations of broken bonds and to a lesser degree the exterior basal facets are the main active surface of kaolinite that influences the sorption power.

Thus, the following conclusions can be drawn on the basis of the study of the structural and crystal-chemical particularities of kaolinite:

- the degree of ordering and particle-size of kaolinite decrease successively from normal to alkaline kaolin;
- the differences in kaolinite ordering between samples of different types of kaolin and among samples of each type of kaolin are due to the change in the ratio of the sizes of the kaolinite precipitates, i.e., kaolin consists of a mixture of kaolinite of different sizes: large particles with average degree of ordering and small particles, right up to ultrafine, x-ray amorphous particles with low ordering;
- higher EHC intensity is characteristic for normal and gneiss kaolins as compared with alkaline kaolin.

It can be supposed that the low ordering of kaolinite, which is due to, first and foremost, small crystal sizes, as well as the high EHC intensity in a complex determine its high sorption power (Table 2).

**Material Composition of Different Types of Kaolin, Factors Resulting in a Change of Microstructure and Ratio of Types of Interparticle Contacts.** The material composition is a sensitive indicator of kaolin formation. Different combinations of types of contacts, the character and area of individual contacts as well as their number are important indicators of kaolin microstructure on which the strength and rheological properties of kaolin depend. The material composition reflects the effect of different abiotic (wetting – drying; freezing – thawing) and biochemical (biota activity) processes occurring in the weathering crust and with aging rocks in mines, leading to a change of the material composition.

Together with clayey minerals — kaolinite with the average ordering, halloysite with different water content, and smectite, which all form the basis of kaolin — ZLD kaolin contains an x-ray amorphous, inorganic component, organic compounds, and biota (differing by the composition of the metabolites and mechanism of their action).

The natural microflora of ZLD kaolin is represented by aerobic heterotrophic, denitrifying and iron-reducing bacteria. The presence of organic acids in the kaolin (formates, acetates, lactates, and others), which are potential donors for microbial metabolism, attests to microbial activity [9, 27 – 29]. Bio-accessible Fe (III), which is an electron acceptor, is present in all kaolin samples [28]. In the presence of organic and mineral components in the kaolin, the microflora give rise to the formation of new chemical and biochemical systems in the direction of development of gley genesis [24]. As ZLD kaolin is moistened, the medium is initially weakly alkaline with  $\text{pH} = 8$ , while the redox state is moderately reducing with redox potential  $pe = 3.0 - 3.5$ , and these values gradually decrease during aging. Depending on the wetting time, a transition occurs from an aerobic to anaerobic state with products of metabolism being released.

Theoretically, disaggregation of clayey particles can occur in a definite period of time solely due to a change in moisture content and temperature without any participation of biota. However, in moistened kaolin, the functioning of the biota accelerates the process of particle disaggregation and peptization of clayey minerals due to the action of the metabolites, some of which — the organic acids — act as surfactants while others — mineral and organic acids — dissolve inorganic amorphous compounds and weakly crystallized minerals cementing the particles [9, 27]. The multiplicity of abiotic and biochemical processes occurring can be reduced to three main effects on kaolin: disaggregation of particles and dispersing of the minerals to dissolution, migration of Si, Al, and Fe in the form of a suspension and their reprecipitation on the walls of pores and on the surface of aggregates. The biochemical processes result in destruction of aggregates and, correspondingly, reduction of the average size of kaolinite particles and the appearance of active centers on them. As the kaolin dries out, depending its wetting time, a new microstructure with elevated density and low intra-aggregate porosity can form.

Different chemical and physical methods are used for diagnostics of ultrafine and amorphous components of kaolin. Selective dissolution is used mainly to identify and perform quantitative determination of the amorphous inorganic compounds (aluminosilicate gels and iron oxides) and poorly crystallized clayey minerals. The most commonly used method is Tamm extraction ( $\text{pH} = 3.3$ ) [9, 27, 30]. As the elements Si, Al, and Fe migrate into the Tamm solution the values for ZLD kaolin (over 29 samples) 0.20 – 5.90, 0.10 – 2.30, and 0.30 – 1.60 mg/liter, respectively, exceed the values for Prosyanskovskoe kaolin and Latnenskoe and Chasov-Yar clays but are much lower than the values for

Troshkovskoe clay (54.5, 20.5, and 3.50 mg/liter). These data suggest that the large size of the aggregates, especially characteristic for alkaline kaolin, is due to the presence of weakly crystallized and amorphous components, cementing small particles of kaolinite and halloysite into aggregates, whose presence electronic microscopy confirms.

Probably, this explains the discrepancy between the data on the microaggregate state of kaolin and the sizes of the kaolinite crystals in different types of kaolin. On average, the sizes of the aggregates of alkaline kaolin are larger than the aggregates of normal kaolin, but the kaolinite crystals in alkaline kaolin are smaller than the crystallites in normal kaolin.

When the moisture content of kaolin changes, depending on the composition of the material the types of interparticle contacts change in a regular manner. Three types of contacts can form: coagulation, condensation, and phase. The coagulation and condensation contacts predominate between the clayey particles; these contacts are weak and their breakdown is reversible. In a water condensation medium, condensation contacts can change into coagulation contacts and be restored as they dry out. The thixotropic behavior of kaolin is based on the properties of these coagulation contacts. The phase contacts are characterized by a substantial contact area between the mineral particles or the development of a new phase strongly binding the particles into microaggregates.

ZLD kaolin differs by the presence of, together with coagulation and condensation interparticle contacts, two types of phase contacts: crystallization contacts formed by iron oxides and cementation contacts formed by aluminosilicate gels. These types of contacts differ by their properties: non-swelling, weakly crystallized iron oxides, interacting with clayey minerals, modify their surface to some extent and are not dissolved by sodium pyrophosphate, so that aggregates do not breakdown — on the contrary, aluminosilicate gels, possessing an amorphous structure, sorb a great deal of water and are weakly dissolved by sodium pyrophosphate. For this reason, when kaolin samples are prepared according to GOST 23905 these microaggregates break down only partially.

The relative ratios of the contact types change continually as the sample-preparation conditions change. For example, when preparing kaolin samples for determining the ultimate bending strength the kaolin must be moistened to a plastic state and the samples must be kept for a definite period of time in the moistened and dry states. As the samples dry out, the more coarsely disperse alkaline kaolin shows greater shrinkage and ultimate bending strength as compared with the granite kaolin (see Table 2). For example, the average values of the ultimate bending strength and shrinkage are 1.85 MPa and 4.3% for type-A kaolin samples and 3.16 MPa and 5.5% for case B<sub>2</sub>, respectively. This effect accompanying moistening can be explained by a change in the particle-size ratio toward smaller sizes with coagulation interparticle con-

tacts predominating and the effect accompanying drying out can be explained by the densification of the particles, including a decrease of the intra-aggregate porosity with the coagulation contacts reverting back to condensation and phase contacts.

**Liquefaction and Fluidity of Kaolin Suspensions.** It has been established that ZLD kaolin is difficult to liquefy, because to obtain the first fluidity  $T_1$  of the suspension of kaolin a large amount of liquid glass is required, as compared with, for example, Glukhovetskoe kaolin with similar moisture content.

The fluidity of a kaolin suspension with moisture content 50% was determined after the suspension was allowed to stand for 30 sec (first fluidity  $T_1$ ) and 30 min (second fluidity  $T_2$ ) in a VZ-246 viscometer with a 5 mm in diameter opening and addition of liquid glass. One-hundred fifty four kaolin samples were selected to determine the fluidity.

Among 79 normal kaolin samples 41 possess first and second fluidity with thickening factor  $T_1/T_2$  corresponding to the requirements established, 12 samples possess only first fluidity and the remaining 26 have no fluidity. Only nine of 75 samples of alkaline kaolin possess first and second fluidity, all others do not. Therefore, for at least half the normal kaolin samples and most of the alkaline kaolin samples the kaolin suspension has no fluidity while part of the samples possessing first fluidity have no second fluidity, i.e., when kept standing the suspension thickens. Hence, a structured disperse system forms in the kaolin suspension — a transition occurs from a freely disperse to a bound disperse system with properties specific to it: the viscosity increases and the system loses its fluidity. These properties are determined by the nature of the contacts taking account of the chemical nature, shape, and surface state of the particles of the disperse phases and by the dispersity, degree of anisometricity, and concentration of the particles in the dispersion medium [31].

All these necessary conditions and criteria for the formation of structured disperse systems were found while analyzing the experimental data on the structure and properties of ZDL kaolin. In the first place, alkaline kaolin as compared with normal kaolin consists of larger aggregates with a different ratio of the types of contacts: coagulation, condensation, and phase. In a kaolin suspension, abiotic and biochemical processes develop; their flow is confirmed by a change of the redox potential in model experiments with a kaolin suspension, the phase contacts break down and the ratio of the types of contacts changes as does the particle-size distribution with the particles becoming smaller, right down to the formation of ultrafine particles. As a result of the breakdown of the interparticle contacts the number of particles per unit volume increases, so that the viscosity of the suspension will increase considerably. In the second place, with respect to the degree of structural ordering kaolinite in alkaline kaolin is characterized as medium-perfect: as compared with kaolinite of normal kaolin the indices  $\chi_R$  and  $\chi_{EPR}$  have lower values and therefore the concentration of defects is higher. This fac-

tor increases the force and energy of interaction in the interparticle contacts, so that the critical concentration at which a structural network starts to form in the entire volume of the disperse system decreases. In the third place, in the presence of particles of anisometric shape, such as, in particular, elongated plates of kaolinite, halloysite in the form of short stick-like particles to tubular crystals or particles of illite, the critical concentration giving rise to structuring of the disperse system decreases sharply.

Thus, the regulation of the liquefaction and fluidity of a suspension of ZLD kaolin is based on a change in the contribution of factors and conditions impeding the formation of a structured disperse system. The following methods are most effective:

- the dry method of enriching green kaolin, making it possible to divide kaolin according to fractions and find a ratio of kaolin particles with different size fractions, including a limit on the content of particles smaller than 1  $\mu\text{m}$  [8];

- comprehensive use of, together with soda and liquid glass, organic liquefiers such as a carbon-alkaline reagent and sodium polyacrylates; as a result of their action the volume of the water adsorbed by kaolin decreases and the volume of free water increases in the total volume of the kaolin suspension [2, 8];

- hydrothermal processing of kaolin, which has a structure-modifying effect on kaolins: the fraction of particles larger than 10–20  $\mu\text{m}$  and < 1  $\mu\text{m}$  decreases; the crystallinity index of kaolinite increases; the strength of single contacts decreases and therefore the amount of liquefying additive decreases, the conditionally statistical and conditionally dynamic ultimate fluidity decrease;

- aging of moist green kaolin on open surfaces, changing the periods of its freezing-thawing states followed by enrichment according to an established technological scheme; it was shown that after the green kaolin is allowed to age the micro-aggregate composition of kaolin changes, and the amount of halloysite and the thickening factor decrease;

- drying of green kaolin for kaolin enrichment at higher temperature (> 200°C), which corresponds to the conditions of heat-treatment in the presence of vapor as compared with drying in a softer regime (about 100°C) and results in shorter first fluidity time and lower thickening factor of the kaolin suspension.

## REFERENCES

1. R. A. Platova, A. A. Shmarina, and Z. V. Stafeeva, "Multidimensional colorimetric gradation of kaolin," *Steklo Keram.*, No. 1, 17–22 (2009); R. A. Platova, A. A. Shmarina, and Z. V. Stafeeva, "Multidimensional colorimetric gradation of kaolin," *Glass Ceram.*, **66**(1–2), 17–22 (2009).
2. G. N. Maslennikova, N. V. Kolyshkina, A. S. Shamrikov, and Z. V. Stafeeva, "Enriched kaolin from the Zhuravlinyi Log for ceramic production," *Steklo Keram.*, No. 1, 15–19 (2002); G. N. Maslennikova, N. V. Kolyshkina, A. S. Shamrikov, and Z. V. Stafeeva, "Concentrated kaolin from the Zhuravlinyi Log for ceramic production," *Glass Ceram.*, **59**(1–2), 17–21 (2002).
3. E. I. Evtushenko and O. K. Sysa, "Structural modification of clayey raw material under hydrothermal conditions," *Izv. Vyssh. Uchebn. Zaved., Severo-Kavkazskii Region, Tekhnicheskie Nauki*, No. 2, 82–86 (2006).
4. T. M. Argynbaev, Z. V. Stafeeva, and R. A. Platova, "Kaolin and quartz from the Zhuravlinyi Log deposit," in: *Ceramics and Refractories: Prospective Solutions and Nanotechnologies: Reports at an International Conference with Elements of a Scientific School for Youth* [in Russian], Izd. BGUTU, Belgorod (2010), pp. 39–44.
5. B. F. Gorbachev, G. P. Vasyanov, V. I. Kakorin, and V. P. Luzin, "Kaolins and sericites from the Plastovskoe kaolin region (Chelyabinsk Oblast)," *Litologiya Polez. Iskopaemye*, No. 2, 187–200 (2007).
6. E. B. Belogub, "Use of a x-ray diffractometry and thermogravimetry system for evaluation of kaolin raw material," in: *Minerals: Structure, Properties, Methods of Investigation* [in Russian], URO RAN, Miass, Ekaterinburg (2010), pp. 24–26.
7. R. F. Giese, "Kaolin minerals: structures and stabilities," *Rev. Mineral. Geochem.*, **19**(1), 29–66 (1988).
8. A. S. Shamrikov, *Technology for the Enrichment and Stabilization of the Ceramic Properties of Kaolins from the Zhuravlinyi Log Deposit, Author's Abstract of Candidate's Thesis* [in Russian], Tomsk (2002).
9. Yu. N. Vodyanitskii, *Diagnostics of Overmoistened Mineral Soils* [in Russian], GNU Pochvennyi Institut im. V. V. Dokuchaeva, Moscow (2008).
10. N. S. Bortnikov, R. M. Mineeva, V. N. Novikov, and S. V. Sobolev, "Influence of the size effect on the crystal-morphological properties of kaolinite according to electron microscopy and EPR data (Zhuravlinyi Log Deposit, Southern Urals), *Dokl. Akad. Nauk*, **439**(2), 240–243 (2011).
11. T. A. Sokolova, T. Ya. Dronova, and I. I. Tolpeshta, *Clayey Minerals in Soils* [in Russian], Grif i K, Tula (2005).
12. G. I. Kovalev and D. I. Levin, "On the particularities of kaolins differing by the degree of kaolinite crystallinity," in: *Collection of Scientific Works* [in Russian], GIKI, Leningrad (1977), Issue 1(54), pp. 3–24.
13. P. Aparicio and E. Galan, "Mineralogical interference on kaolinite crystallinity and iron content," *Clays Clay Minerals*, **47**(1), 12–27 (1999).
14. M. M. Mestdagh, L. Vielvoye, and A. J. Herbillon, "Iron and kaolinite; the relationship between kaolinite crystallinity and iron content," *Clay Minerals*, **15**(1), 1–13 (1980).
15. E. Balan, Th. Allard, B. Boizat, G. Morin, and J.-P. Muller, "Structural  $\text{Fe}^{3+}$  in natural kaolinites: new insights from electron paramagnetic resonance spectra fitting at X and Q band frequencies," *Clays Clay Minerals*, **47**(5), 605–616 (1999).
16. B. Clozel, T. Allard, and J.-P. Muller, "Nature and stability of radiation-induced defects in natural kaolinites: new results and a reappraisal of published works," *Clays Clay Minerals*, **42**(6), 657–666 (1994).
17. D. N. Hinckley, "Variability in 'crystallinity' values among the kaolin deposit of the coastal plain of Georgia and South Carolina," *Clays Clay Minerals*, **11**(1), 229–235 (1962).
18. G. N. Maslennikova, K. A. Kuvshinova, and Yu. T. Platov, "Structural-phase changes of iron-containing impurities in the process of porcelain formation," *Steklo Keram.*, No. 12, 11–14 (1997); G. N. Maslennikova, K. A. Kuvshinova, and Yu. T. Platov, "Structural-phase changes of iron-bearing impurities in the process of porcelain formation," *Glass Ceram.*, **54**(11–12), 390–393 (1997).

19. J.-M. Gault, P. Ermakoff, Th. Allard, and J.-P. Muller, "Paramagnetic  $\text{Fe}^{3+}$ : a sensitive probe for disorder in kaolinite," *Clays Clay Minerals*, **45**(4), 496 – 505 (1997).
20. N. S. Bortnikov, R. M. Mineeva, and S. V. Soboleva, "Paramagnetic centers  $\text{Fe}^{3+}$  on the surface of kaolinite particles," *Dokl. Akad. Nauk*, **422**(1), 85 – 87 (2008).
21. R. A. Platova, V. A. Rassulov, and A. A. Shmarina, "Identification of mineral impurities in kaolin and kaolin-based porcelain by luminescence spectroscopy," in: *Abstracts of Reports at the International Scientific Conference on Fedorov Lectures* [in Russian], Moscow (2008), 293 – 295.
22. Th. Delineau, Th. Allard, J.-P. Muller, et al., "Ftir reflectance vs. EPR studies of structural iron in kaolinites," *Clays Clay Minerals*, **42**(3), 308 – 320 (1994).
23. N. S. Bortnikov, R. M. Mineeva, I. M. Novikov, et al., "Iron in kaolinites of the kaolin and bauxite-bearing crusts of weathered granites according to EPR data," *Dokl. Akad. Nauk*, **423**(6), 1 – 4 (2008).
24. V. A. Grevtsev, *Mineralogical-Technological Evaluation of the Quality of Non-Metallic Minerals by Radiospectroscopy, Author's Abstract of Doctoral's Thesis* [in Russian], Kazan (2011).
25. W. J. Kingery (ed.), *Ceramic Production Processes* [Russian translation], Inostr. Lit., Moscow (1960), pp. 36 – 44.
26. Ma Chi and R. A. Eggleton, "Cation exchange capacity of kaolinite," *Clays Clay Minerals*, **47**(2), 174 – 180 (1999).
27. R. A. Platova and G. N. Maslennikova, "Biochemical nature of gley formation during aging of clay materials," *Steklo Keram.*, No. 9. 14 – 20 (2009); R. A. Platova and G. N. Maslennikova, "Biochemical nature of gley formation during aging of clay materials (review)," *Glass Ceram.*, **66**(9 – 10), 318 – 323 (2009).
28. E. S. Shelobolina, S. M. Pickering, and D. R. Lovley, "Fe-cycle bacteria from industrial clays mined in Georgia, USA," *Clays Clay Minerals*, **53**(6), 580 – 586 (2005).
29. E. S. Turova, *Microbial Transformation of Kaolins and Kaolin-Containing Raw Materials, Author's Abstract of Candidate's Thesis* [in Russian], Moscow (1997).
30. T. V. Vakalova and V. M. Pogrebenkov, "Clay raw materials in the Siberian region," *Steklo Keram.*, No. 12, 23 – 27 (2002); T. V. Vakalova and V. M. Pogrebenkov, "Agrillaceous materials in the Siberian region," *Glass Ceram.*, **59**(11 – 12), 409 – 413 (2002).
31. N. B. Ur'ev, "Structured disperse systems," *Sorovskii Obrazovatel'nyi Zh.*, No. 6, 42 – 47 (1998).